

# ANALYSIS OF RESIDUUM DEMETALATION BY SIZE EXCLUSION CHROMATOGRAPHY WITH ELEMENT SPECIFIC DETECTION

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## ABSTRACT

We analyzed thermally treated heavy residua by element specific size exclusion chromatography (SEC-HPLC-ICP) to elucidate the fate of the V and Ni compounds. Thermal treatment, in addition to removing metals, significantly reduces the size of the remaining metal-containing compounds.

We thermally treated the distillable and nondistillable metals separately. The distilled metals, primarily porphyrins, were completely processed out. The nonvolatile metals, which constituted most of the Ni and V, were either removed, or reduced in size.

When treating heavy residua over commercial fixed-bed hydroprocessing catalysts, the metal-containing molecules in the size range of the catalyst pore are preferentially removed. Those larger than the pore size appear to demetalate more slowly.

The results argue demetalation is a function of the ligand structure and size of the metal-containing species and not the coordination sphere around the metal center.

## INTRODUCTION

High metals content is one of the inhibiting factors in the processing of heavy crudes and residua. These metals, particularly V and Ni, are deleterious to fixed bed catalysts, causing deactivation (1).

New technology has recently been developed to process feeds with high metals contents. This technology centers around metals removal by using high metals loading catalyst or guard beds (2), or separation and rejection of poor quality high metals materials (3).

Understanding the mechanism, or mechanisms, by which these metals are removed can ultimately lead to better processing methods. But we are limited by the methods of examination for metals. The inorganic compounds are at ppm levels, which lead to particularly difficult analytical problems. To circumvent this, we have developed and applied size exclusion chromatography, with inductively coupled plasma emission spectroscopy (SEC-HPLC-ICP) to examine V and Ni as a function of process conditions. This technique allows monitoring the size environment of a selected element, without the complications of other components.

## EXPERIMENTAL

We obtained California atmospheric residua (AR) No. 1 and No. 2 by single plate distillation of the corresponding crude to a 343°C cut-point. Both AR are high in metals having over 400 ppm Ni + V.

The thermal processing was performed in a tubular flow reactor, under high hydrogen partial pressure. The fixed-bed catalytic processing was performed over commercially available metals loaded alumina catalysts at typical hydroprocessing conditions. The samples were collected from the reactors and stored cold, under nitrogen, until use. Care was taken to protect the samples from oxygen, and to analyze them as soon after processing as possible.

The processing conditions were selected based on the apparent thermal reaction threshold temperature of 410°C (see discussion below). Treatment at and above this temperature is referred to thermal processing. Three standard severities were chosen -- low, moderate, and high. Fixed-bed catalytic treatment was done below this temperature.

The fractionation of the California AR No. 1 into a porphyrin-containing distillate cut (454°C to 677°C) and a nonporphyrin-containing residuum (677°C+) was performed using a short-path distillation apparatus (DISTACT). The cut point between the two fractions was based on the earlier results on metals distribution as a function of boiling point [M. M. Boduszynski unpublished results].

We analyzed both feeds and products by SEC-HPLC-ICP. The technique and the equipment have been described in detail previously (4). The feeds and products were prepared and analyzed by the following procedure:

- 1) dilute the feed or product to a concentration of 1 to 5% by wt mobile phase of o-xylene, o-cresol, and pyridine.
- 2) elute the solution by HPLC on Ultragel 50 and 1000 nm analytical columns.
- 3) detect emission profiles of V (292.40 nm) and Ni (231.60 nm) using an ICP source.

The output, or response profile so obtained, measures the selected elemental content as a function of the elution time. Calibration with polystyrene (PS) standards (4) and model compounds (5,6), changes the response profile from a time domain to a logarithmic size domain. Because we are interested in the relative distribution, and not absolute changes, the profiles shown here are not normalized to absolute metals content.

The porphyrin/nonporphyrin separation methods are also reported elsewhere (4). UV-vis determinations were performed on alumina and capped-silica column separated fractions by techniques discussed elsewhere (4,7).

#### METAL STRUCTURES IN THE FEEDS

Figure 1 shows the V and Ni SEC-HPLC-ICP response profiles for California AR No. 1. The V profile exhibits the typical bimodal distribution seen for many other crudes and residua (4-6,8,9). The profiles are generally bimodal in distribution, with maxima at MW around 800 and 9000 (PS standards). The maximum at 800 has been assigned by extraction techniques to be metallopetroporphyrins (4). For the crudes examined, the metallopetroporphyrins are most of the small metal compounds, but account for only a minor amount of the

metals in the crude. 26% and 34% of the V is bound as petroporphyrin for California AR No. 1 and No. 2 respectively.

We believe the remaining metal-containing compounds are nonporphyrins. We have examined, the average first coordination sphere around the V in the nonporphyrin fraction using electron paramagnetic resonance (EPR) spectroscopy, and have found various combinations of N, S and O. For California AR No. 2, the nonporphyrin coordination sphere is N O 2S (9).

The Ni SEC-HPLC-ICP profile in Figure 1 exhibits more noise due to the lower response factor of Ni in the ICP determination in comparison with V, and the lower concentration of Ni in the feed. It also shows that there are far fewer Ni porphyrins than V porphyrins, as observed for other crudes and residua (5,6). We discuss the following results using only the V profiles. Ni profiles behaved similarly in all cases.

These results and extraction data (6) have lead to a formulation of models for metals in crude oils. We believe the metals to be of two types: 1) the porphyrins which have a narrow, but well defined molecular weight range due to homologous series substitutions (10), and 2) the nonporphyrins, which span a much broader molecular weight and size range. The nonporphyrin molecular size range could be due to small molecular weight compounds which are convoluted in a tertiary-agglomerated structure. The nonporphyrins could also have homologous series type structure.

#### THERMAL PROCESSING: TEMPERATURE BEHAVIOR

Figure 2 exhibits the V response profiles for California AR No. 1 thermal products. These products were generated from processing in a tubular reactor at moderate thermal severity and low thermal severity. The profiles correspond to 78% and 38% V removal, respectively.

At moderate thermal severity, the remaining metal compounds exhibit a dramatic shift to smaller molecular sizes. The larger prominent maximum is shifted from its position in the feed and appears to be vanadyl petroporphyrins. This will be discussed in a subsequent section.

At low thermal severity, the remaining metal-containing compounds exhibit similar trends, but shift much less than in the moderate thermal severity case.

These results combined with high thermal severity product profiles (not shown), indicate the extent of size reduction appears to be a function of the thermal reactor temperature.

#### THERMAL PROCESSING: REACTION TIME EFFECT

Figure 3 shows California AR No. 2 processed at moderate thermal severity in the tubular reactor for different reaction times. V removal was 70% in the long residence time, and 50% in the short residence time. There is little difference in the profile distribution of these products. Liquid residence time appears to have little effect on the amount of size reduction.

### CATALYTIC PROCESSING

California AR No. 1 was processed downflow in a fixed-bed reactor over commercially available hydroprocessing catalysts. The V SEC-HPLC-ICP profiles of products from short residence times and long residence times are shown in Figure 4. The short residence time profile corresponds to 50% V removal. The remaining metal-containing compounds exhibit a conspicuous lack of smaller components. The porphyrin and similar size compounds are absent, while some of the larger, nonporphyrin compounds are still evident.

Fixed-bed processing at long residence time also removes the smaller metal-containing compounds. The long residence time profile corresponds to 70% V removal. The profile is very similar to that of the short residence time profile showing the longer reaction time does not appear to affect the size profile of the remaining metal-containing compounds. This is also seen in the thermal treatment results above.

Under fixed-bed processing conditions, the catalyst pore size appears important. The compounds that are in the size range of the catalyst pore are removed. This behavior has been seen in the studies on the processing of Safaniya asphaltenes (11), Arabian Light vacuum residuum (VR) asphaltenes and maltenes (12), in gel permeation chromatography (GPC) studies of Venezuelan crudes (13), and in demetalation kinetic studies of Boscan and Arabian Light residua (14).

The metal-containing compounds which do not fit in the catalyst pores require more severe processing. Longer residence times were required to remove these metals. The kinetics of metals removal over typical hydrosulfurization catalysts have been determined in some cases to be second order (15). This has been explained as demetalation by two different first-order rate constants (16). These could be the respective demetalation rates for the metals which can fit into the catalyst pores and those which cannot.

### THERMAL PROCESSING: PORPHYRINS AND NONPORPHYRINS

To determine the individual fates of the porphyrins and nonporphyrins during processing, California AR No. 1 was separated into distillable and nondistillable metal fractions by distillation, and each fraction was thermally processed. Figure 5 shows the separation by distillation. The 454°C to 677°C fraction shows only small size metal-containing compounds. The V in this fraction was determined by UV-vis spectroscopy to be 98% porphyrin, and by methanol extraction to be 90% porphyrin. The 677°C+ fraction is primarily the nonporphyrin metal compounds. Methanol extraction indicates only 2% of the V bound as porphyrin, and UV-vis spectroscopy indicates only 2% of the V bound as porphyrin in this fraction.

For thermal treatment at moderate thermal severity both fractions were diluted with appropriate vacuum gas oil components to their original metals concentration in the AR. Figure 6 shows the V SEC-HPLC-ICP profiles of the 454°C to 677°C fraction before and after processing. It is clear from the profiles that the porphyrins are completely removed (as well as the rest of the V).

Figure 7 shows the V SEC-HPLC-ICP profiles for the 677°C+ fraction before and after moderate thermal severity treatment. The remaining metal-containing compounds are shifted to the smaller

molecular size, similar to those of the moderate thermal severity processing of California AR No. 1.

Nonporphyrins have been thought of as porphyrins which have been encapsulated in an agglomerative network (17). They would not necessarily be detected as porphyrins because their spectroscopic and physical properties could be changed by this agglomeration. The size reduction seen in the thermal treatment of the 677°C+ cut produces compounds which are smaller than either the feed petroporphyrins, or porphyrin model compounds, as evidenced in Figure 7. Porphyrin extraction and UV-vis determination show less than 3% of the V is bound as petroporphyrin in this product. We feel this verifies the existence of the nonporphyrins which are not encapsulated porphyrins.

This argument would be nullified if the structure of the metal-containing compounds were sufficiently changed during processing. For example, the porphyrins could be demetalated, but instead of falling out completely, the metals could combine with other polar organic molecules and could rebind having a nonporphyrin ligand environment.

#### DISCUSSION

The results shown here are important in the overall picture of processing residua and heavy oils. Although little data exists on the behavior of the metal-containing compounds monitored by element specific detection, some studies have been done by other techniques.

GPC studies on the organic portion of Arabian Light VR maltenes and asphaltenes thermally processed under vis-breaking conditions showed a dramatic decrease in the average molecular size (12) upon increase of process temperature. The same results were found in the heat treatment of Safaniya VR asphaltenes (11). This agrees well with our thermal processing results for the Ni and V, where we also see size reduction which is dependent on thermal temperatures.

The effect of fixed-bed processing under catalytic conditions has been studied more thoroughly. Arabian Light treated under mild hydroprocessing conditions exhibited metals reduction corresponding to catalyst pore size (14). Similar results for the organic portion have been seen with Arabian Light VR asphaltenes (12), Morichal crude (13), and asphaltenes from Safaniya VR (11). This also agrees well with our fixed-bed processing results where the metals are distinctively affected by the pore size of the catalyst.

One of the important consequences of this study is that the porphyrins appear to be removed first in residuum demetalation. This conclusion has been reached previously. Porphyrins have been found to be preferentially removed in thermal treatment with hydrogen and/or hydrogen sulfide (18). In addition, the reaction threshold temperature for porphyrin demetalation was 400°C without, but only 200°C with a fixed-bed hydrogenative catalyst. Oxidative treatment studies of residua have also shown the same effect -- the porphyrins come out first (19,20).

Our studies support these conclusions. The results from separate processing of the porphyrins and the nonporphyrins are evidence that the porphyrins are the most labile. In addition, the removal of the metals is greatly assisted by the fixed-bed hydroprocessing catalyst, which operates at a substantially lower temperature.

However, it is important to note that these results may not be a consequence of the porphyrin or the nonporphyrin coordination sphere, but simply a consequence of the size of the compounds. In the thermal case, the porphyrins were removed because they were most of the smallest metal-containing molecules. In the fixed-bed processing, the porphyrins were removed because of the metal-catalyst pore size relationship.

Studies of feeds and products from the ABC process (21), showed the isotropic EPR parameters of the vanadyl ion exhibited little change in processing, and therefore little or no change in the first coordination sphere about the metal center (22,23). It was concluded from this that the reactivity of the vanadium is determined by the macrostructure of the residuum, and not by the nature of the coordinating metal ligands.

This is also supported by the rates of hydrodemetalation studies of extracted petroporphyrins. The facility by which hydrogenation of porphyrins (24) occurs strongly argues the rate of demetalation is not a function of the intrinsic reaction rate of the first coordination sphere around the metal ion, but diffusion through or denaturing of the polar medium around the metal-centers.

#### CONCLUSION

We have examined thermal processing and catalytic fixed bed processing by SEC-HPLC-ICP to determine demetalation mechanisms. Thermal processing removes Ni and V and reduces the size of the remaining metal-containing compounds. Fixed-bed processing removes metals as a function of the pore size.

By separating the porphyrins from the nonporphyrins, we have found the porphyrins process the easiest under thermal conditions. This could be a result of their intrinsic reactivity, or merely a function of size or macrostructure. It is our contention, the macrostructure is rate controlling for at least the nonporphyrins.

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FIGURE 1  
SEC-HPLC-ICP PROFILES FOR  
CALIFORNIA AR NO. 1

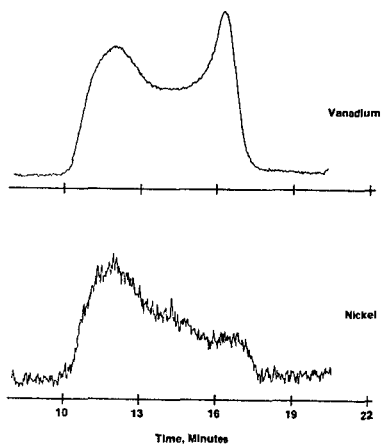


FIGURE 2  
CHANGES IN VANADIUM DISTRIBUTION FROM  
THERMAL TREATMENT OF CALIFORNIA AR NO. 1

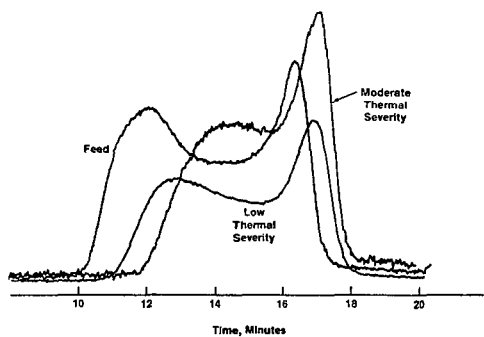


FIGURE 3  
CHANGES IN VANADIUM DISTRIBUTION FROM  
THERMAL PROCESSING OF CALIFORNIA AR  
NO. 2 AT DIFFERENT RESIDENCE TIMES

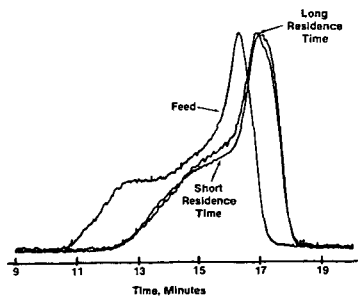




FIGURE 4  
CHANGES IN VANADIUM DISTRIBUTION FROM  
FIXED-BED TREATMENT OF CALIFORNIA AR NO. 1 AT  
DIFFERENT RESIDENCE TIMES

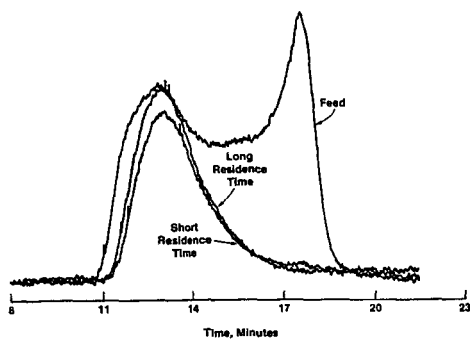


FIGURE 5  
VANADIUM SIZE PROFILES OF CALIFORNIA AR NO. 1,  
454°C to 677°C DISTILLATION CUT, 677°C+ RESIDUE

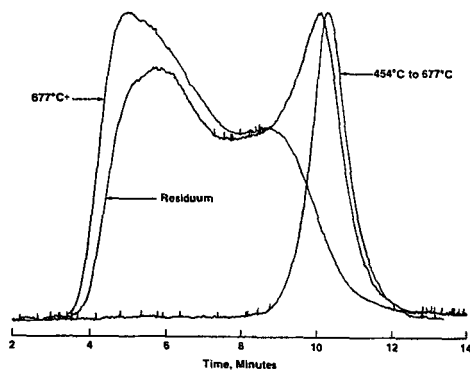


FIGURE 6  
CHANGE IN VANADIUM SIZE DISTRIBUTION OF THE  
454°C to 677°C DISTILLATION CUT OF CALIFORNIA  
AR NO. 1 UPON THERMAL TREATMENT

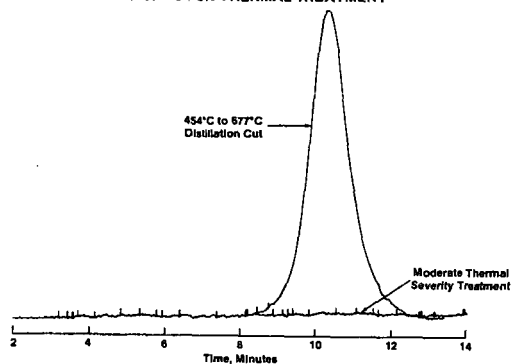
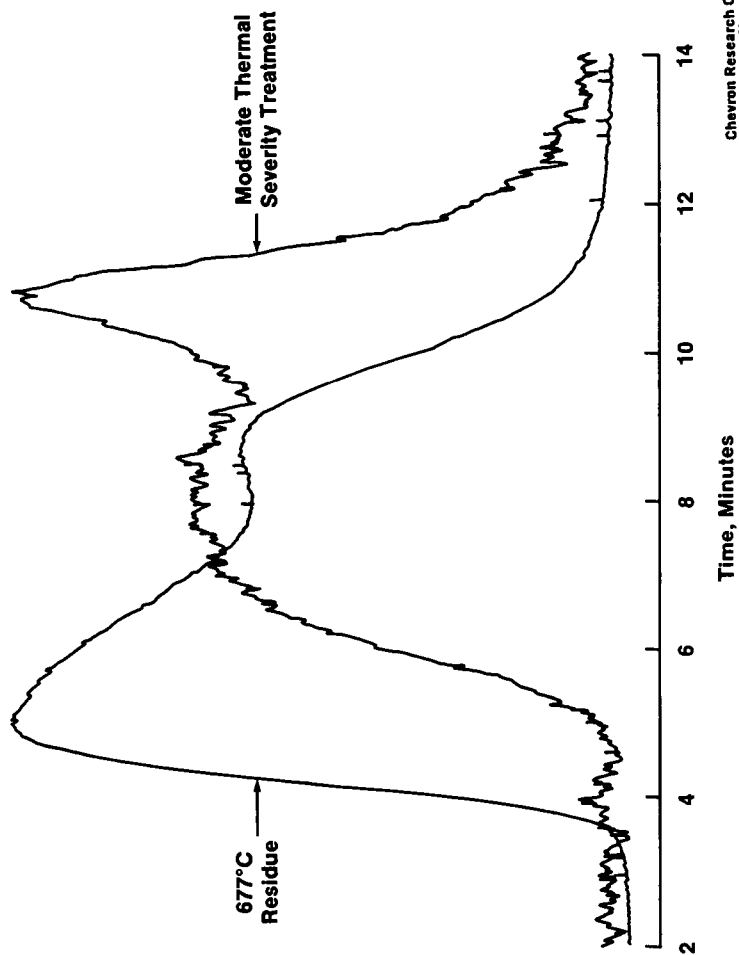


FIGURE 7

CHANGES IN VANADIUM SIZE DISTRIBUTION OF THE  
677°C+ RESIDUE OF CALIFORNIA AR NO. 1  
UPON THERMAL TREATMENT



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